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Methane emissions from UK estuaries: Re-evaluating the estuarine source of tropospheric methane from Europe

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ABSTRACT

We report measurements of dissolved methane (CH_4) and turbidity in axial surveys of six UK inner estuaries between February 2000 and October 2002: the Humber, Forth, Tamar, Tyne, Tees, and Tay. Dissolved CH_4 was always supersaturated relative to air and strong spatial and temporal variability was a notable feature. Super-saturation was highest in the Tyne (max. 107,725%; mean 26,348 ± 30,330%) and lowest in the Tay (max. 1294%; mean 584 ± 425%). All six inner estuaries were atmospheric CH_4 sources throughout their surveyed reaches. Broad mid-estuarine CH_4 maxima were characteristic of all inner estuaries except the Tay and are consistent with substantial CH_4 inputs from intertidal flats. In the Humber, Forth and Tay maximal CH_4 in the low salinity turbidity maximum zone (TMZ) implied additional large CH_4 inputs at these locations but overall CH_4 — turbidity relationships were complex, potentially reflecting interactions between CH_4 inputs in the TMZ and from intertidal sediments, with estuarine hydrodynamics. CH_4 flux densities (emissions per unit area) varied over an order of magnitude, some of the highest values occurring in relatively small estuaries (e.g. Tees and Tyne). Evidently overall CH_4 emissions from inner estuaries are disproportionate to area extent. Combining our measurements with all relevant published data, applying an aerially weighted approach that discriminated between inner and outer estuaries and using a revised estimate of the total European estuarine area, we derived total (inner plus outer) estuarine CH_4 emissions for the UK and Europe as follows: UK, $5.8 \pm 5.8 \times 10^9$ g yr^{-1}; Europe (including UK), $2.7 \pm 6.8 \times 10^{10}$ g yr^{-1}. We estimate the individual contributions to these totals from inner and outer estuaries at ~25% and 75% respectively. Our figure for European estuaries is around an order of magnitude lower than an earlier estimate that set this equivalent to 2–13% of total marine CH_4 emissions. Adjusting for our revised estuarine area and for wind speeds that we consider to be more realistic, this comes more into line with our revised synthesis.

1. Introduction

Methane (CH_4) has an atmospheric radiative forcing ~30% of that of CO_2. It influences oxidising capacity, O_3 and OH radical in the troposphere and impacts stratospheric O_3 and H_2O (Hartmann et al., 2013). It has a troposphere half-life of ~9 years and a dry mole fraction, 1803 ± 2 ppbv in 2011 (Hartmann et al., 2013), that has more than doubled since the industrial revolution, due mostly to anthropogenic inputs but also to fluctuations in the balance of natural sources and sinks. Analysis of top–down and bottom–up estimates of tropospheric CH_4 sources sets an annual total of 678 Tg yr^{-1} (range 542–852 Tg yr^{-1}) for the period 2000–2009, of which around 50–65% is anthropogenic (Stocker et al., 2013). The range reflects uncertainties in the fractional contributions from individual sources and a tendency for bottom up approaches to overestimate the natural source total (Kirschke et al., 2013). While the latest IPCC synthesis discusses marine CH_4 emissions only in terms of hydrate leakage (5–10 Tg yr^{-1}) and seeps (~20 Tg yr^{-1}) (Stocker et al., 2013), coastal marine ecosystems including estuaries may also make a significant contribution (Borges and Abril, 2011). Estuaries link coastal waters with terrestrial aquatic systems and because the latter may be important sources of tropospheric CH_4 (Bastviken et al., 2011; Borges et al., 2015), estuaries are implicated in the emission of this freshwater-derived CH_4 to air. Indeed, estuarine CH_4 principally arises from these freshwater inputs along with in situ sediment methanogenesis, although additional localised production associated with high water column turbidity was proposed for two UK estuaries (Upstill-Goddard et al., 2000). Estuarine CH_4 super-saturations >20,000% have frequently been reported (e.g. Upstill-Goddard et al., 2000; Abril and Iversen, 2002; Middelburg et al., 2002) but much higher super-saturations have occasionally been found (e.g. Ferrón et al., 2010).

In this paper we present dissolved CH_4 distributions and estimates of atmospheric CH_4 emissions for six UK inner estuarine systems of varying sizes and anthropogenic impact; five along the North Sea Coast (Humber, Forth, Tyne, Tees, and Tay) and one in the Western English Channel

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(Tamar). By analogy with a similar analysis that we recently completed for dissolved N_2O using the same samples (Barnes and Upstill-Goddard, 2011), we have incorporated these and previously published data into a re-evaluation of the tropospheric CH_4 contribution from UK estuaries and from estuaries in the UK and mainland Europe combined.

2. Study area

The major physical characteristics of our study estuaries (Forth, Humber, Tamar, Tay, Tees, and Tyne: Fig. 1) are summarised in Table 1 and are described in some detail in Barnes and Upstill-Goddard

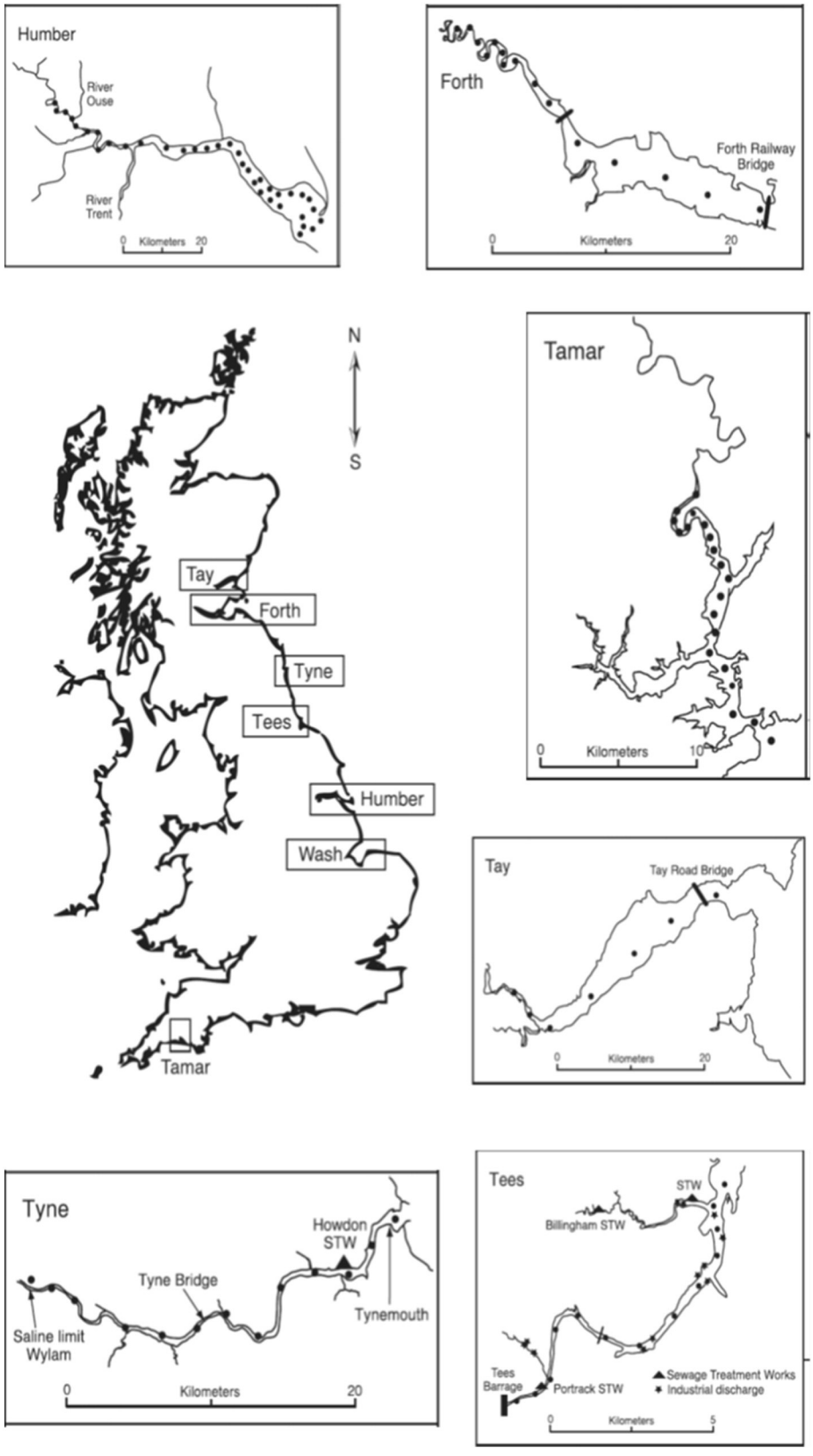

Fig. 1. Locations of six UK inner estuaries. Sampling stations are indicated by the black dots.

Table 1
Physical and chemical characteristics of six UK inner estuaries (Barnes and Upstill-Goddard, 2011).

Estuary	Area (km^2)	Mean freshwater input ($m^3\ s^{-1}$)	Mean tidal range (m)	Tidal/Mixing regime	Salinity range	Residence time (days)	Maximum surface SPM ($mg\ l^{-1}$)
Humber	303.5	250	5.7	Macrotidal/well mixed	0–34	30–60	>30,000
Forth	84.0	66	3.8	Macrotidal/well mixed	0–34	7–30	~7000
Tamar	39.6	27	3.5	Macrotidal/well mixed	0–34	2–10	~300
Tay	121.3	200	3.8	Macrotidal/partially-well mixed	0–34	2–11	~200
Tees	13.5	12	3.2	Mesotidal/stratified/partially mixed	0–34	1	<100
Tyne	7.9	25	3.2	Mesotidal/partially-well mixed	0–34	3–10	~600

(2011). For purposes of clarity in our subsequent data analysis and discussion, we refer to them throughout this paper as "inner estuaries", as in our earlier synthesis for N_2O (Barnes and Upstill-Goddard, 2011). Inner estuaries are dominated by tidally driven turbulent mixing, have large salinity gradients and their trace gas emissions may be anthropogenically influenced. In contrast "outer estuaries" (sometimes referred to as "river plumes") have restricted salinity ranges but they may cover large areas subject to high wind stress and have uncertain trace gas emissions.

In brief, our inner estuaries (total area: 570 km^2) span a range of physical scales and degrees of anthropogenic impact (Barnes and Upstill-Goddard, 2011). Together they account for around a quarter of the total UK inner estuarine area and almost 10% of the European inner estuarine area, drain >20% of the UK mainland and account for ~13% of total UK freshwater discharge (Barnes and Upstill-Goddard, 2011). In four of our inner estuaries (Forth, Humber, Tamar, Tyne) tidal asymmetry (flood tide velocity > ebb tide velocity) 'pumps' marine suspended particulate matter (SPM) upstream and traps it along with river borne SPM in a turbidity maximum zone (TMZ) at low salinity, especially during summer spring tides when river discharge is low (Uncles and Stephens, 1993). In the Forth, Humber and Tamar the TMZ is especially well-defined in summer but in the Tyne it is much more diffuse even though maximum SPM is somewhat higher than in the Tamar (Table 1); this is because Tyne SPM has a more even spatial distribution. High levels of both free and particle-attached bacterial activity in the TMZ (Plummer et al., 1987; Crump and Baross, 1996) and enhanced particle residence times typically lead to reduced O_2 (Balls, 1992) and the consequent processing of trace gases and other biogeochemical components in the TMZ (Abril et al., 2000; Upstill-Goddard et al., 2000; Barnes and Upstill-Goddard, 2011).

3. Methods

3.1. Sampling

Full sampling details are presented in Barnes and Upstill-Goddard (2011). In brief, a 4.7 m rigid inflatable boat (RIB: Avon Seasport) was used. Relevant dates are listed in Table 2. Surveys commenced at or near the mouth of each estuary and as far as was possible, terminated just upstream of the limit of saline intrusion at local high water. Water samples were collected at 1 m depth (Richter & Wiese 2.5 L water sampler). Vertical profiles of salinity, temperature and turbidity were obtained with a CTD (Idronaut 316 with Seapoint OEM turbidity meter), although technical issues with the sensor precluded collecting a complete dataset for turbidity. Typical measurement precisions (1σ) were ±0.01 salinity; ±0.1 °C; ±1% turbidity.

3.2. Dissolved and atmospheric CH_4

Samples for dissolved CH_4 analyses were decanted into 1 L glass volumetric flasks by over filling each by at least one sample volume using a silicon rubber tube, augmented with 200 μL 0.1 M HgCl to arrest microbial activity and sealed with the exclusion of all air. Dissolved gas samples preserved in this way are stable for at least several weeks (Elkins, 1980). All samples were analysed within 48 h of collection. Ambient air collected in 0.1 L gas-tight glass syringes (SAMCO; MRS Scientific,

Table 2
Dissolved CH_4 and CH_4 emissions from 6 inner UK estuaries.

Location	Date	Percent CH_4 saturation			T°C	ΔCH_4 $nmol\ l^{-1}$	Mean monthly wind speed $m\ s^{-1}$	Mean *k* Wanninkhof (1992)	Mean *k* Clark et al. (1995)	Estuarine CH_4 emission ($g\ d^{-1}$)		Salinity range	*n*
		Maximum	Mean	Median						Wanninkhof	Clark		
Humber	07/26/01	4264	1541 ± 1452	994	21.0	1771	4.00 (±2.48)	5.2	6.0	1.1×10^5	1.2×10^5	0–13	17
	09/25/01	5558	1551 ± 1605	1054	13.3	2265	4.69 (±2.90)	7.1	9.0	1.9×10^5	2.4×10^5	0–14	15
	Mean		1546 ± 1473	1054						5×10^5	1.8×10^5		
Forth	10/12/00	13,147	7788 ± 3604	6879	11.1	17,033	5.25 (±3.26)	9.0	11.5	4.9×10^5	6.3×10^5	0–31	10
	04/23/01	6180	2423 ± 2008	1791	8.2	4596	5.05 (±3.13)	8.3	11.8	1.2×10^5	1.7×10^5	0–32	10
	06/20/01	4571	2674 ± 1100	2338	13.5	5286	4.22 (±2.62)	5.8	7.8	1.0×10^5	1.3×10^5	0–33	10
	08/07/01	19,548	8248 ± 4896	6329	18.1	13,170	4.02 (±2.49)	5.2	6.4	2.2×10^5	2.7×10^5	0–30	9
	Mean		5067 ± 4107	4290						2.3×10^5	3.0×10^5		
Tamar	02/05/01	3819	2329 ± 1265	582	7.7	6840	5.15 (±3.19)	8.6	12.4	0.9×10^5	1.3×10^5	0–26	14
	04/27/01	5837	4412 ± 1277	4815	10.4	12,069	6.10 (±3.78)	12.1	14.8	2.2×10^5	2.7×10^5	0–29	15
	Mean		3407 ± 1637	3721						1.6×10^5	2.0×10^5		
Tyne	01/09/00	35,253	15,934 ± 12,774	20,531	6.0	59,100	5.67 (±3.52)	10.4	5.2	1.9×10^5	0.9×10^5	0–34	9
	05/31/00s	39,069	26,162 ± 10,402	22,820	11.6	56,343	5.05 (±3.13)	8.3	10.6	1.4×10^5	1.8×10^5	0–29	10
	09/21/00	64,107	19,046 ± 23,991	9520	8.2	25,601	4.69 (±2.90)	7.1	8.8	0.6×10^5	0.7×10^5	0–8	11
	09/29/00	107,725	73,931 ± 29,025	86,373	12.9	206,900	4.69 (±2.90)	7.1	9.2	4.5×10^5	5.8×10^5	0–24	12
	10/06/00	8704	5570 ± 3004	6461	11.9	15,652	5.25 (±3.26)	10.6	8.6	0.5×10^5	0.4×10^5	0–22	9
	08/01/02	8593	5904 ± 2249	6337	12.4	15,150	5.00 (±3.10)	8.1	11.6	0.4×10^5	0.5×10^5	0–11	9
	Mean		26,348 ± 30,330	11,371						1.6×10^5	1.7×10^5		
Tees	02/22/01	15,382	7466 ± 4353	7928	6.2	22,513	5.10 (±3.16	8.6	13.0	1.0×10^5	1.5×10^5	20–33	11
	06/05/01	38,431	21,718 ± 13,480	27,048	12.6	65,796	4.22 (±2.62	5.8	8.0	2.0×10^5	2.7×10^5	16–31	11
	07/18/02	52,368	21,365 ± 15,928	16,246	14.2	37,476	4.01 (±2.49	5.2	7.0	1.0×10^5	1.4×10^5	22–33	9
	Mean		16,559 ± 13,474	10,378						1.3×10^5	1.9×10^5		
Tay	04/05/01	1294	584 ± 425	396	8.0	809	5.04 (±3.13)	8.3	11.9	0.3×10^5	0.5×10^5	0–34	6

UK)) was transferred to a series of glass vials with butyl self-sealing septa (12 cm^3 Vacutainers, Isochem, UK). An additional exhaust needle prevented over pressurization. Care was taken to always sample upwind of the RIB to minimise the possibility of contamination. CH_4 analysis was by single phase equilibration gas chromatography (Shimadzu GC14-B) with flame ionisation detection (120 °C). For full details see Upstill-Goddard et al. (1996). In brief, chromatographic separation (80–100 mesh Porapak-Q®) was at 60 °C. Primary calibration used certified CH_4 standards of 8.5 ppmv and 5.2 ppmv (both ±1%) in ultra-high purity (UHP) N_2 (Air Products, UK). Routine calibrations used two secondary CH_4 standards (1.5 ppmv and 2.5 ppmv) prepared from the primary standard by pressure dilution in UHP N_2 and with estimated accuracies ~±1.5% (Upstill-Goddard et al., 1996). Overall analytical precisions, established via multiple analyses ($n = 15$) of the secondary standards, is better than ±1%.

3.3. Sea-to-air CH_4 emissions

We estimated sea-to-air CH_4 emissions from $F = k_w L\Delta p$, where F is the flux (mol m^{-2} d^{-1}), k_w is the transfer velocity of CH_4 (cm h^{-1}), L is CH_4 solubility (mol cm^{-3} atm^{-1}) (Wiesenburg and Guinasso, 1979), and Δp is the CH_4 sea-to-air partial pressure difference; for this we used the mean CH_4 mixing ratio of all of our atmospheric air measurements (2230 ± 130 ppbv; n = 131). The range of these values was 1920–2400 ppbv, similar to the ranges found for other European inner estuaries (Middelburg et al., 2002) but somewhat higher than in adjacent outer estuaries and marginal seas (Bange et al., 1996). Considering the very large CH_4 super-saturations in estuaries, such variability in atmospheric CH_4 does not measurably affect our CH_4 emissions estimates.

Deriving meaningful estimates of air–sea gas exchange for shallow macrotidal inner estuaries is a substantial challenge because published parameterizations give up to five-fold variability in k_w (e.g. Clark et al., 1994, 1995; Carini et al., 1996; Kremer et al., 2003; Zappa et al., 2003; Borges et al., 2004). Although Ho et al. (2011a) suggested that open-ocean parameterisations (e.g. Nightingale et al., 2000; Ho et al., 2011b) may be adequate for some large rivers/estuaries (e.g. Hudson), it should be noted that in addition to wind speed, turbulence due to tidal currents can exert an important control on gas exchange in smaller shallow estuaries (Zappa et al., 2003; Borges et al., 2004), as are found in the UK and Europe. Borges et al. (2004) devised a k_w parameterisation involving both tidal currents and wind speed but its requirement for water depths and current speeds precludes its use here because these data are unavailable for our inner estuaries.

Noting the inherent uncertainties, we therefore used the k_w—wind speed relations of Wanninkhof (1992) and Clark et al. (1995) to estimate CH_4 emissions. Both have been widely applied, which facilitates comparison with other systems, and the latter was derived for a tidal river-estuary. Using Wanninkhof (1992) returns higher k_w values than do other open ocean relations for the same wind speed (e.g. Nightingale et al., 2000; Ho et al., 2011b). Its use therefore sets an upper limit to emissions estimates based on such open ocean relations. In both cases we scaled the resulting k_w estimates (for CO_2 at 20 °C in seawater and freshwater respectively) to CH_4 at in situ temperature, using Schmidt numbers from Wanninkhof (1992). Wind speeds were obtained from the British Atmospheric Data Centre (http://nerc.ac.uk). Monthly averages for the survey periods are for the nearest meteorological station to each estuary and the uncertainty in these data is expressed as the standard deviation (1σ) of the average value in each case. This procedure is identical to that used to estimate N_2O emissions from our studied estuaries (Barnes and Upstill-Goddard, 2011).

4. Results

Table 2 lists maximum, mean and median dissolved CH_4 saturations along with ΔCH_4 (= LΔp), the dissolved excess CH_4 concentration relative to atmospheric equilibrium (~0.002–0.003 μM), for all six inner estuaries. A full data listing is in Table S1. The observed ranges of dissolved CH_4 saturation are similar to those found previously in these and other European inner estuaries (Table 3).

Fig. 2 shows dissolved CH_4 vs salinity. All samples were super-saturated in CH_4. Evidently all of these inner estuaries are strong sources of atmospheric CH_4 throughout their accessible reaches. Strong spatial and temporal variability is a notable feature of the data; maximum, mean and median saturations, and consequently ΔCH_4, all spanned two orders of magnitude, both between and within the individual inner estuaries. The highest absolute CH_4 (107,725%; 207 μM) and the highest mean CH_4 (73,931 ± 29,025%; 142 ± 56 μM) were in the Tyne and the lowest corresponding values (1294%, 35.3 μM; 584 ± 425%, 16 ± 12 μM) were in the Tay. Overall these inner estuarine CH_4 distributions all showed some similarities to the corresponding distributions of dissolved N_2O (Barnes and Upstill-Goddard, 2011) but there were some important differences. A major feature of all inner estuaries except the Tay is a broad mid-estuarine maximum in which CH_4 saturations were generally highest in summer. In an earlier study of the Humber and Tyne we partly attributed such features to CH_4 inputs via intermediate river endmembers (Upstill-Goddard et al., 2000). In general however, for the Forth, Humber, Tamar and Tyne these maxima are most likely dominated by diffusive CH_4 inputs from the extensive areas of intertidal mudflats that are a characteristic feature, the seasonal differences being consistent with temperature control of the rate of sediment methanogenesis. For the Tamar this conclusion is broadly supported by earlier work that applied a one-dimensional analogue mixing model to link mid-estuarine water column maxima for a range of dissolved constituents, similar in shape to those we observed for CH_4, to benthic fluxes (Knox et al., 1981, 1984, 1986; Upstill-Goddard and Elderfield, 1988). Although the CH_4 distribution in the Tees is rather similar to those in these other inner estuaries (Fig. 2), we note that salinity in the Tees is largely independent of geographical position because of substantial freshwater inputs associated with 15 major anthropogenic sources, including 3 sewage treatment works (Barnes, 2003). Consequently, the observed CH_4 distributions are likely to be measurably influenced by these inputs, a conclusion that we also reached for dissolved N_2O and NH_4^+ (Barnes and Upstill-Goddard, 2011). For the Tyne a CH_4 mass balance previously allowed us to rule out any measurable impact on dissolved CH_4 from a large mid-estuarine sewage outfall because sewage pre-treatment reduces effluent-associated CH_4 to ambient levels (Upstill-Goddard et al., 2000).

In the Humber and Tay and in one survey in the Forth, dissolved CH_4 was maximal close to the freshwater–saltwater interface (salinity <0.5) (Fig. 2). The Humber and Forth both have pronounced TMZ's at these locations (Balls et al., 1996; Uncles et al., 1999) and the steep seaward decrease in CH_4 towards salinities ~1–2 is also characteristic of dissolved N_2O and NO_3^- in the same surveys (Barnes and Upstill-Goddard, 2011). We consistently observed a low salinity CH_4 maximum during six earlier surveys of the Humber covering an annual cycle and also in a single survey of the Tyne (Upstill-Goddard et al., 2000). In both cases these maxima (Humber, 6000–21,000%; ~190–670 nM; Tyne, 21,800%; ~650 nM) greatly exceeded measured river water values, implying a large in situ supply of dissolved CH_4 in both inner estuaries. To explain these features we invoked either CH_4 release from anoxic underlying sediments during particle resuspension, in situ water column production via methanogenesis on tidally re-suspended particles, or some combination of the two (Upstill-Goddard et al., 2000). Although turbidity is not available for all surveys due to technical issues, the available data show overall positive relationships between CH_4 and turbidity, for single surveys in the Humber and Tamar and for two out of three surveys in each of the Forth and Tyne (Fig. 3). In contrast, in the Forth survey of June 2001 there was no clearly discernible trend and in one of the Tyne September 2000 surveys we observed a strong negative trend. This is perhaps not surprising given that we previously inferred a complicated CH_4 vs turbidity relationship in the Tyne

Table 3
Dissolved CH_4 and CH_4 emissions for inner and outer European Estuaries.

Type	Location	Date(s)	Mean CH_4 (Percent saturation)	Median CH_4 (Percent saturation)	Saturation range (percent)	Area km^2	Annual CH_4 emission ($g\ CH_4\ yr^{-1}$)	CH_4 flux density ($g\ CH_4\ m^{-2}\ yr^{-1}$)	Remarks	Reference
Inner	Humber, UK	Jul 2001 to Sep 2001	1546	1054	194–5558	303.6	6.6×10^7	0.2	Seasonal study	This study
	Forth, UK	Dec 2000 to Jul 2012	5067	4290	627–19,548	84.0	10.9×10^7	1.3	Seasonal study	This study
	Tamar, UK	Feb 2001 to Apr 2001	3407	3721	452–5837	39.6	7.3×10^7	1.8	Seasonal study	This study
	Tyne, UK	Jan 2000 to Aug 2002	26,348	11,371	599–107,725	7.9	6.2×10^7	7.9	Seasonal study	This study
	Tees, UK	Feb 2001 to Jul 2002	16,559	10,378	1702–52,368	13.5	4.0×10^7	3.0	Seasonal study	This study
	Tay, UK	Apr 2001	584	396	234–1294	121.3	3.1×10^7	0.3	Single survey	This study
					Total	569.9	38.1×10^7			
	Douro, Portugal	Sep 1998		3610	620–5720	2			Single survey	Middelburg et al. (2002)
	Elbe, Germany	May 1994			700–2200	327			Single survey	Rehder et al. (1998)
	Elbe, Germany	Apr 1997		580	130–2980	327			Single survey	Middelburg et al. (2002)
	Ems, Germany	Jul 1997		3150	920–13,100	161			Single survey	Middelburg et al. (2002)
	Gironde, France	Oct 1996-Feb. 1998		580	70–13,400	442			Seasonal study	Middelburg et al. (2002)
	Guadalquivir, Spain	Nov 2006			150–1740			2.9	Seasonal study	Burgos et al. (2015)
	Guadelete, Spain	Feb 2013 to Nov 2013	21,753		1105–130,358				Single survey	Ferrón et al. (2010)
	Humber, UK	Nov 1995 to Dec 1996		3641	248–21,048	303.6	4.8×10^7	0.2	Seasonal study	Upstill-Goddard et al. (2000)
	Loire, France	Sep 1998		660	340–23,10 0	41			Single survey	Middelburg et al. (2002)
	Ria de Vigo	Apr 2003 to Sept. 2004	1620		101–8500	178	3.1×10^6	0.02	Seasonal study	Kitidis et al. (2007)
	Río San Pedro	Feb to Oct. 2004			514–5000	0.3	1.5×10^5	0.5	Seasonal study	Ferrón et al. (2007)
	Rhine, Netherlands	Oct 1996 to Apr 1998		8400	140–49,700	71			Seasonal study	Middelburg et al. (2002)
	Sado, Portugal	Sept 1998		5900	940–158,000	102			Single survey	Middelburg et al. (2002)
	Scheldt, Netherlands	Jun 1996-Apr 1998		3210	380–20,400	269			Seasonal study	Middelburg et al. (2002)
	Tay, UK	Apr 2009-Jun 2010	2600		100–13,100	121.3	6.9×10^7	1.0	Seasonal study	Harley et al. (2015)
	Temmesjoki, Finland,	May 2003-Aug 2004	17,200		7970–29,800	3	2.7×10^7	9.1	Seasonal study	Silvennoinen et al. (2008)
	Thames, UK	Feb 1999		570	150–6700	225			Single survey	Middelburg et al. (2002)
	Tyne, UK	Jan 1996	5843		450–2000	7.9	1.1×10^7	1.4	Single survey	Upstill-Goddard et al. (2000)
Outer	Amvrakikos Bay	Jul 1993	522 ± 127			~400			Single survey	Bange et al. (1996)
	Bay of Cádiz	Jun 2006-May 2007	1540 ± 330		1080–1820	88			Seasonal study	Ferrón et al. (2010)
	Bodden Waters	Jun 1994 to Apr. 1997	7802		105–15,500	2000			Seasonal study	Bange et al. (1998)
	Elbe Plume (German Bight)	Oct 2010 to Jun. 2012	1000 ± 430		340–1880		3.3×10^9	0.13	Seasonal study	Osudar et al. (2015)
	Danube Plume (Black Sea)	July 1995	5340		15,800–54,500	25,000			Single survey	Amouroux et al. (2002)
	Eckernförde Bay	Feb 1993 to May 1994			162–2460	51	$0.5–102 \times 10^6$	0.01–2.0	Seasonal study	Bussman and Suess (1998)
	Gulf of Lions	Jun 1998	22,506	16,440	1400–21,000	17,000			Single survey	Marty et al. (2001)
	Randers Fjord	Feb 2000 to Dec 2000	5800		320–50,520	19.4	$0.3–4.9 \times 10^7$	0.13–2.5	Seasonal study	Abril and Iversen (2002)
	Rhone Plume (Gulf of Lions)	Mar 1997 to Nov 1997	31,750	31,440	15,880–54,520				Seasonal study	Marty et al. (2001)
	Thermaikos Gulf	Apr 1998	28,217	31,720	3840–55,120				Single survey	Marty et al. (2001)
	Wash	Aug 1993	492	498	194–707	666	1.5×10^9	2.3	Single survey	Upstill-Goddard et al. (2000)

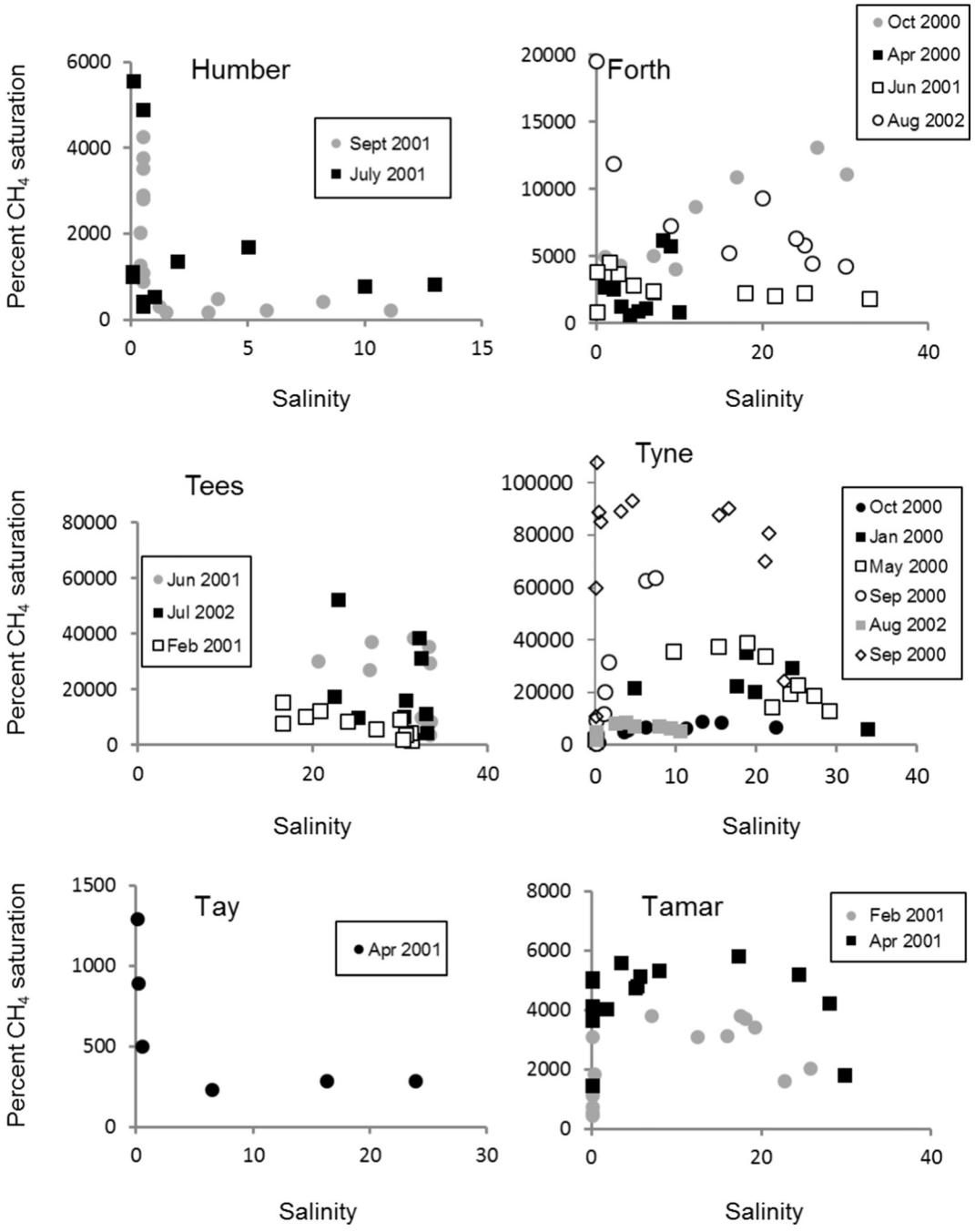

Fig. 2. Estuarine CH_4 saturations vs salinity in the Forth, Humber, Tamar, Tay, Tees and Tyne estuaries.

(Upstill-Goddard et al., 2000) that likely reflects several competing processes. In the Ems, Loire and Gironde inner estuaries Middelburg et al. (2002) found relatively low dissolved CH_4 at high turbidity, for salinities <10, which they ascribed to accelerated CH_4 outgassing due to high turbulence or to increased CH_4 oxidation by SPM-attached bacteria. The latter scenario is supported by CH_4 oxidation rates measured in Gironde TMZ samples (Abril et al., 2007). It is likely that such processes operate to some extent in the Tyne and Forth, and quite possibly at our other study sites, but due to diffusive CH_4 signals from mid-estuarine intertidal sediments inferred earlier and periods of sediment resuspension due to changing hydrodynamics, CH_4 vs turbidity relationships will in all likelihood be temporally variable. It is interesting to note that we previously reported more consistent positive relationships between N_2O and turbidity for some of these inner estuaries (Barnes and Upstill-Goddard, 2011). This is consistent with the finding that N_2O distributions in these inner estuaries are, unlike those of CH_4, dominated by a single process: water column nitrification of NH_4^+ by SPM-associated bacteria at the TMZ.

5. Discussion

5.1. CH_4 emissions from UK inner estuaries

Following reasoning we presented earlier (Barnes and Upstill-Goddard, 2011) our sampling campaign was conceived to give as complete spatial and temporal coverage as was practicable. Nevertheless, due to some technical issues our CH_4 dataset is somewhat less complete than that for N_2O (Barnes and Upstill-Goddard, 2011) and thus gives rather less detailed seasonal coverage (Table 2). In addition, in each of our inner estuaries CH_4 saturation spans a much wider

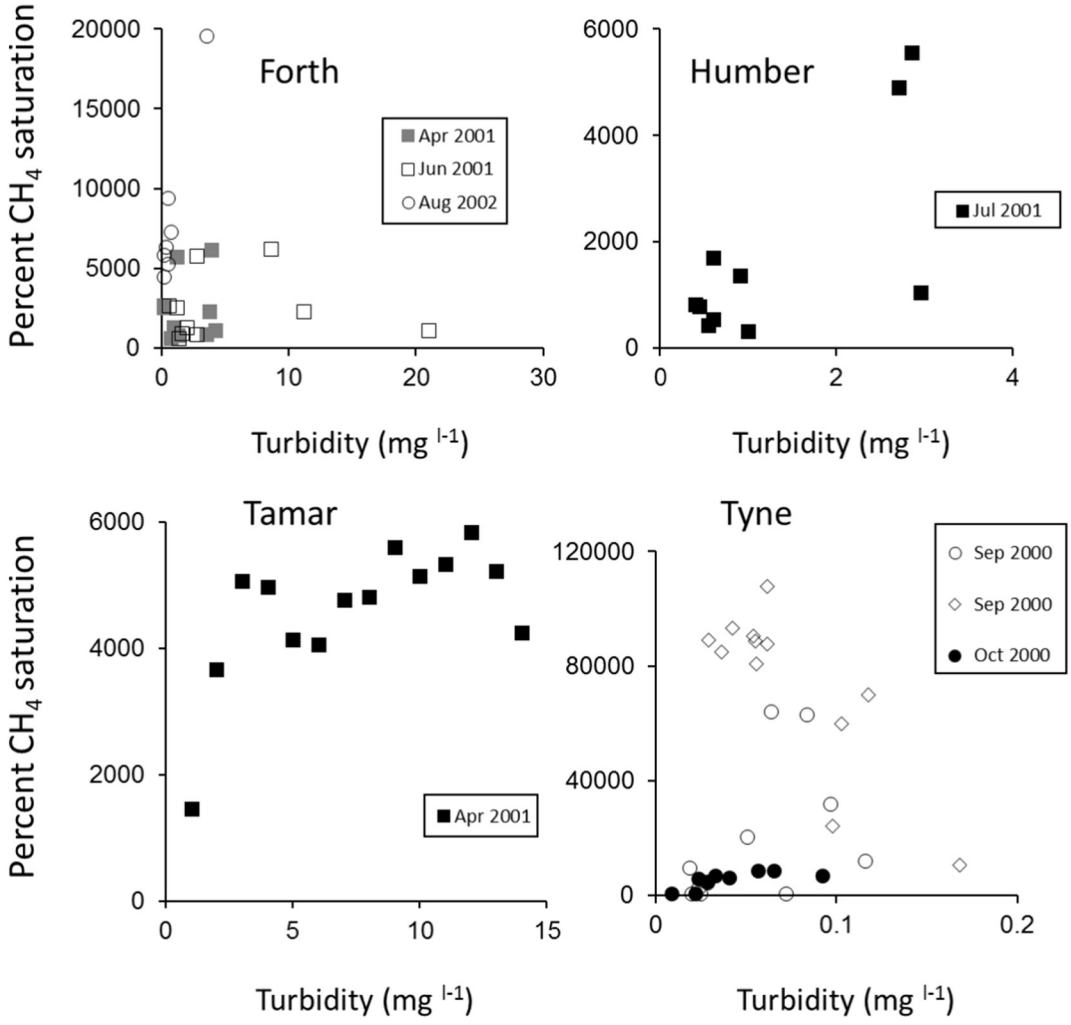

Fig. 3. CH_4 vs turbidity in the Forth, Humber, Tamar and Tyne estuaries. Note the different scales for turbidity.

range than N_2O saturation and unlike our N_2O data, for which we observed non-normal distributions only infrequently, CH_4 was highly non-normally distributed in most of our surveys. Consequently our CH_4 data have comparatively high standard deviations. For N_2O Seitzinger and Kroeze (1998) emphasize that using median rather than mean saturations gives better estimates of estuarine emissions. Notwithstanding the non-normal distributions of CH_4, we report median as well as mean CH_4 in Table 2 and for consistency with our approach for N_2O, we have based our estimates of mean annual CH_4 emissions (Table 2) on the median values. For these various reasons these estimates have inherently higher uncertainty than our corresponding estimates for N_2O (Barnes and Upstill-Goddard, 2011).

We could discern no clear seasonal signal in CH_4 emissions at any of our study sites (Table 2). This is counter to what we found for N_2O, for which summer emissions were clearly the highest in four of the studied inner estuaries (Barnes and Upstill-Goddard, 2011). In part this must reflect the higher uncertainties of our CH_4 flux estimates but it is probably also a result of several processes influencing water column CH_4. Whereas the N_2O distributions in these inner estuaries were essentially dominated by a single process (water column nitrification of NH_4^+), for CH_4 production in the TMZ, benthic inputs from submerged sediments and laterally from exposed tidal flats, along with water column oxidation may all be important. The interaction of these with seasonal signals in estuarine hydrodynamics may well obscure any seasonality in biogeochemical process rates arising from temperature alone. If so, notwithstanding the issues leading to the CH_4 emissions uncertainties outlined above, such complex interactions in hydrodynamically active inner estuaries might to some extent confound attempts to further refine estimates of their annual CH_4 emissions.

CH_4 flux densities (emissions per unit area) varied by up to an order of magnitude, both within and between UK inner estuaries (Table 2). Evidently some of the smaller inner estuaries (e.g. Tyne and Tees) have comparatively high CH_4 flux densities (Table 3), such that inner estuarine total emissions are disproportionate to area extent. Although we found similar behaviour for N_2O in some of these inner estuaries, in contrast the Humber accounted for >93% of the combined total annual N_2O emission from these sites (Barnes and Upstill-Goddard, 2011), which clearly is not the case for CH_4.

Apart from our earlier study of the Humber and Tyne (Upstill-Goddard et al., 2000) we are aware of only one other such UK study for the Tay (Harley et al., 2015; Table 3). Our six study sites are thus the only ones on which to base an estimate of UK inner estuarine CH_4 emissions. Together, they account for ~25% (570 km^2) of the total UK inner estuarine area (2311 km^2) and all of their emissions fall within the range for other European systems, which are rather few in number (Table 3). It is instructive to compare our current estimates for the Humber and Tyne (Table 2) with our earlier estimates for these sites (Table 3), which we derived without applying any assumed gas transfer-wind speed relation but by instead applying a conservative dilution line to the seawater and low salinity CH_4 endmembers to estimate "total CH_4 removal", which we then corrected for oxidation loss (Upstill-Goddard et al., 2000). Given the inherent uncertainties in

both approaches, the agreement between the resulting mean emissions estimates (to factors ~1.4 for the Humber and ~7 for the Tyne; Table 3) is encouraging, especially given that individual emissions estimates for the Tyne spanned an order of magnitude (Table 2). This instils some degree of confidence in these two independent approaches. We also note that our single emissions estimate for the Tay agrees to within a factor ~2 with the mean of the recent more detailed study of Harley et al. (2015).

In our earlier work on N_2O (Barnes and Upstill-Goddard, 2011) our combined inner and outer UK estuarine area of 4205 km^2 (inner estuaries 2311 km^2; outer estuaries 1894 km^2) was obtained from data for 93 mainland UK estuaries (Nedwell et al., 2002). We interrogated its validity by dividing it by the UK coastline length (17,820 km; UK Ordnance Survey) and comparing the result with a similar analysis for US North Atlantic coast estuaries (Woodwell et al., 1973). The agreement between the two gave us confidence in our UK area estimates (Barnes and Upstill-Goddard, 2011). By contrast, a recent typological analysis of nearshore systems (Dürr et al., 2011) gives 7362 km^2 for UK estuaries. This derives from a database for 163 individual systems (DEFRA, 2008) but it does not distinguish inner from outer estuaries. The sum of the areas provided by DEFRA (2008), however, is 5646 km^2 and it seems unclear why the estimate of Durr et al. (2011) is so much larger. Notwithstanding this discrepancy the DEFRA (2008) data include >500 km^2 of non-UK mainland estuaries (mostly Northern Ireland and Western Isles) and some coastal regions covering large areas that are difficult to define in "outer estuarine" terms (e.g. North Norfolk Coast). Taking account of these issues and the attendant uncertainties, and in order to maintain consistency with our earlier emissions estimates for N_2O (Barnes and Upstill-Goddard, 2011), we have followed our earlier protocol, multiplying the sum of the individual mean CH_4 emissions for our study sites (3.87×10^8 g yr^{-1}; Table 3) by the ratio of the estimated UK inner estuarine area (2311 km^2; Nedwell et al., 2002), which includes both open water channels and regions of intertidal sediment, to that of our studied inner estuaries (570 km^2). The resulting total annual CH_4 emission from UK inner estuaries is 1.57×10^9 g (9.81×10^7 mol).

5.2. The combined CH_4 emission from UK inner and outer estuaries

We could find no CH_4 data for UK outer estuaries other than our own from the Wash (Table 3), the surface area of which (666 km^2; Table 3) is ~35% of the UK outer estuarine total (1894 km^2; Nedwell et al., 2002). We therefore applied the same upscaling procedure to the Wash data as for the inner estuaries, to give a total annual CH_4 emission from UK outer estuaries of 4.26×10^9 g (2.66×10^8 mol). Summing the two estimates, the combined annual CH_4 emission from UK inner and outer estuaries is 5.83×10^9 g (3.64×10^8 mol), the respective contributions from inner and outer estuaries being 25% and 75%.

The ratio of the total inner to total outer UK estuarine areas represented in Table 3 (0.85) is close to the UK average (0.82; Nedwell et al., 2002) and we thus consider our combined emission estimate to be quite robust. Absent from the analysis however are large inner estuaries such as the Severn estuary, which has a surface area (556 km^2) that alone accounts for ~24% of the UK total but for which no CH_4 data exist. Given that it has a similar nutrient loading to the Humber (Nedwell et al., 2002) and that both are macrotidal, similar per unit area CH_4 emissions for the two might reasonably be expected. The UK outer estuarine area is dominated by a relatively small number of systems. Adding Morecambe Bay (455 km^2), the Solway Firth (420 km^2) and the Moray Firth (92 km^2) to the Wash (666 km^2) accounts for ~86% of the total, but as for the Severn no CH_4 data are available for these systems.

To set our estimate of the CH_4 flux from UK inner and outer estuaries into context, it is only ~0.25% of the total estimated UK release inventory of 2.3 Tg for the year 2013 (http://naei.defra.gov.uk/data/), all which is classified as anthropogenic and for which >94% is accounted for by enteric fermentation, waste management and fossil fuel combustion. For comparison the UK estuarine contribution is somewhat less than is attributed to UK grassland management but is slightly higher than the total CH_4 production by UK-based chemicals industries for example.

5.3. Reassessing the tropospheric CH_4 source from European estuaries

There are far fewer estimates of CH_4 emissions from European inner and outer estuaries than there are dissolved concentration measurements (Table 3). Nevertheless, the available data imply that although outer estuaries are generally weaker emitters of CH_4 per unit area than are inner estuaries, they may dominate total overall emissions due to their comparatively large surface areas (Table 3). This is in contrast to N_2O, for which the total estimated emission from European outer estuaries was almost three times smaller than that from European inner estuaries (Barnes and Upstill-Goddard, 2011).

The most comprehensive prior synthesis of CH_4 in European estuaries sets a total emission ~0.35 Tg yr^{-1} (range: 0.29–0.63 Tg yr^{-1}), from a combined inner and outer estuarine area ~160,000 km^2 (Bange, 2006). Applying this to a total marine CH_4 emission estimated at 5–15 Tg yr^{-1} (Denman et al., 2007) gives a 2–13% contribution from European estuaries. However, we recently downward revised the combined area of European inner and outer estuaries to ~34,000 km^2 (inner estuaries 6500 km^2; outer estuaries 27,500 km^2) by combining the surface area: coast length ratio for UK estuaries with the total length of UK mainland coastline (Barnes and Upstill-Goddard, 2011). This, along with subsequently published data and our emissions estimates for UK inner estuaries (Table 3), requires that the estimate of Bange (2006) be reconsidered. Middelburg et al. (2002) carried out extensive CH_4 surveys in nine European estuaries (Douro, Elbe, Ems, Gironde, Loire, Rhine, Sado, Scheldt, Thames; Table 3). Although they did not estimate individual estuarine emissions they did derive a median emission for all nine of 0.76 g CH_4 m^{-2} yr^{-1}. Scaling to their combined area (1631 km^2) gives an annual CH_4 emission of 1.2×10^9 g. Adding our estimates for UK inner estuaries and for other European inner estuaries for which emissions data are available (Table 3), gives a CH_4 emission of 1.6×10^9 g yr^{-1} (1.0×10^8 mol yr^{-1}) from a combined total area of 2382 km^2, i.e. from ~37% of our revised European inner estuarine area (6500 km^2). Recognising the attendant uncertainties that arise because contributions from other large European inner estuaries are unknown, we have nevertheless up-scaled this estimate to give a total CH_4 emission ~4.4×10^9 g yr^{-1} (2.8×10^8 mol yr^{-1}) from European inner estuaries. As for the UK, CH_4 emissions estimates for outer estuaries of mainland Europe are few. The only CH_4 emission comparable in magnitude to that from the Wash derives from the work of Osudar et al. (2015) on the Elbe plume in the German Bight (Table 3). These authors do not specify a plume area but based on total dissolved nitrogen distributions in the German Bight that derive from river input (Claussen et al., 2009) we estimate that this could be as much as 5000 km^2. If so, the total emission from an outer estuarine region ~5700 km^2 (Wash plus Elbe plume) could be ~4.8×10^9 g yr^{-1}. Upscaling this to an outer estuarine area of 27,500 km^2 gives ~2.3×10^{10} g yr^{-1}. Finally, adding the contribution from inner estuaries gives a total CH_4 emission from European estuaries ~2.7×10^{10} g yr^{-1} (1.7×10^9 mol yr^{-1}). For comparison we previously estimated a CH_4 emission ~1×10^{10} g yr^{-1} (~6.6×10^8 mol yr^{-1}) for estuaries bordering the southern North Sea (Upstill-Goddard et al., 2000).

Our revised estimate of the combined CH_4 emission from European estuaries is more than an order of magnitude smaller than that of Bange (2006), which was based on a total estuarine area ~5 times larger, did not separate inner and outer estuarine areas, used the arithmetic mean of the individual CH_4 saturations observed in all of the estuaries considered and applied a mean wind speed of 9 m s^{-1}. In our earlier work on N_2O (Barnes and Upstill-Goddard, 2011) we discussed the potential for bias in this approach due to the potential inclusion of anomalously high saturations from individual estuaries and we proposed that a more realistic wind speed might be ~5 m s^{-1} based on

observations in a number of UK estuaries and in the Scheldt. Substituting the latter reduces the emissions estimate of Bange (2006) by a factor of around 3 based on the Wanninkhof (1992) and Clark et al. (1995) relations. Taking all of these issues into account thus brings our emissions estimate and that of Bange (2006) closer together.

5.4. Uncertainty in the estimated the CH_4 emissions

It is important to acknowledge the major sources of uncertainty in our emissions estimates. We previously considered these in some detail for N_2O and that analysis is applicable here, but it is nevertheless valuable to review some important aspects in the current context. In addition to scaling errors relating to the robustness of the area estimates discussed earlier, additional uncertainties relate to how representative the chosen estuaries are of those in the UK and Europe, the selected gas transfer relations and wind speeds, which together define the applied k_w values, potential bias in the selected median values of CH_4 and the possible contribution from CH_4 ebullition which we did not quantify. We conservatively ascribed a ±50% uncertainty to our estimate of the UK inner estuarine area (Barnes and Upstill-Goddard, 2011) and taking account of the data of Durr et al. (2011) and DEFRA (2008) does not materially affect this. Similarly, we ascribe a maximum uncertainty of ±300% to our estimate of the European outer estuarine area, which is necessarily less robust due to difficulties in defining plume edges (Barnes and Upstill-Goddard, 2011). We note however that in contrast to N_2O for which inner estuaries dominated emissions, the effect of this uncertainty is more marked for CH_4, for which 75% of the total emission could arise in outer estuaries.

k_w—wind speed relations are empirical fits with intrinsic uncertainties compounded by the selected wind speeds (Upstill-Goddard, 2006). For the mean wind speeds in our inner estuaries (4.0–6.1 m s^{-1}; Barnes and Upstill-Goddard, 2011) the ratio of k_w derived from Clark et al. (1995) to k_w derived from Wanninkhof (1992) was ~0.89–1.03, whereas for the Wash (7.21 m s^{-1}; Barnes and Upstill-Goddard, 2011) it was 1.16. Considering wind speed variability, the ratio of the standard deviation in wind speed to the mean value over the whole UK was 0.62 (http://www.wind-power-program.com/wind_statistics.htm) for all sampling campaigns (Barnes and Upstill-Goddard, 2011). This exerts maximum uncertainties on k_w ~40–60%, for the wind speed relations used.

Estimating the uncertainty in the CH_4 saturation values used in the emissions estimates is less straightforward than for N_2O, for which unlike CH_4 the saturations were largely normally distributed. We thus conservatively estimate an associated uncertainty of ±50% for CH_4, as compared to ~ ± 20% for N_2O (Barnes and Upstill-Goddard, 2011).

Gas exchange estimates based on turbulent diffusion exclude any contribution to CH_4 emissions from ebullition. Although CH_4 ebullition fluxes may be several-fold higher than diffusional fluxes under some circumstances, especially where high temperatures and high rates of organic matter sedimentation coincide (Ostrovsky, 2003; Barnes et al., 2006; Nirmal Rajkumar et al., 2008) they are difficult to quantify due to high spatial and temporal variability. Even so, ebullition was not observed during any of our surveys, although it should be noted that in tidally energetic regimes it might be rather difficult to identify.

Considering the individual errors above, we estimate a maximum uncertainty in our CH_4 emissions estimates ~ ± 100% for UK estuaries, ~ ± 150% for European inner estuaries ~ ± 300% for European outer estuaries and ~ ± 250% for European estuaries overall (inner plus outer). We thus constrain our estuarine CH_4 emissions as follows: UK (outer plus inner) $5.8 \pm 5.8 \times 10^9$ g yr^{-1}; European (outer plus inner and including UK), $2.7 \pm 6.8 \times 10^{10}$ g yr^{-1}.

6. Conclusions

We re-evaluated total CH_4 emissions from UK inner and outer estuaries and refined previous such estimates for European estuaries using an approach that we believe to be as rigorous as is possible based on currently available data. For the UK, combined inner and outer estuarine emissions contribute only around 0.25% of the national CH_4 emissions inventory. In contrast to our previous conclusions regarding N_2O, outer estuaries may dominate estuarine CH_4 emissions on both the UK and the wider European scales. Even so, the total CH_4 emission from European inner and outer estuaries, including the UK, may be somewhat smaller than was previously believed. We recommend that any future sampling campaigns should specifically target large European outer estuaries for which no CH_4 data are currently available. Doing so should help to further improve the CH_4 emission estimate we have derived.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marchem.2016.01.010.

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